A LAYER SYSTEM COMPRISING A SILICON LAYER AND A PASSIVATING
LAYER, A METHOD FOR PRODUCING A PASSIVATING LAYER ON A SILICON
LAYER AND THEIR USE

The present invention relates to a layer system comprising a
silicon layer and a passivating layer, a method for producing
a passivating layer on a silicon layer and the use of this
layer system or of this method according to the species
defined in the independent claims.

Background Information

According to a method known, for example, from DE 44 20 962 C2
for producing self-supporting MEMS structures in silicon (MEMS
5   = "microelectromechanical structures") by a combination of
anisotropic and isotropic etching techniques, so-called
trenches or deep structures having vertical side walls are
initially anisotropically etched into a silicon substrate
using a reactive plasma. Once the desired etching depth is
10   achieved, then, following a longer passivating step for
depositing a Teflon-like film, a longer etching step is

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performed, during which first a Teflon polymer that formed on the etching ground of the trench is removed by ionic bombardment and subsequently the self-supporting MEMS structures to be produced are isotropically undercut. During

5   this isotropic undercutting, the vertical side walls of the trenches are protected from an etch attack by the previously applied Teflon-like film. According to DE 44 20 962 C2, the isotropic undercutting of the MEMS structures produced proceeds in the silicon substrate material on a purely

10   time-controlled basis.

For depositing the Teflon-like film, a fluorohydrocarbon having a fluorine to carbon ratio that is as low as possible, preferably 2:1, is preferably used, fluorohydrocarbons such

15   C_4F_6, C_5F_8, C_4F_8 or C_3F_6 being particularly suitable for this purpose. A process gas that generally etches isotropically and that provides fluorine radicals, such as SF6, is preferably used for etching silicon.

20   DE 198 47 455 A1 proposes to limit isotropic undercutting vertically with the aid of buried oxide layers. Particularly, according to the document, an etch attack on the MEMS structures is prevented by an intermediate oxide separating the MEMS structure from a sacrificial layer made of silicon.

25   Moreover, the document describes how, instead of using fluorine radicals from a plasma discharge, isotropic undercutting can also be performed using spontaneously and plasmalessly silicon-etching fluorine compounds such as XeF_2, ClF_3 or BrF_3. Following adsorption and chemisorption on a

30   silicon surface, these compounds spontaneously split off fluorine radicals, which results in an isotropic etching removal of the silicon through the formation of silicon tetrafluoride. At the same time there is a very high selectivity vis-à-vis non-silicon materials such as

35   Teflon-like passivating layers or passivating layers of other

compositions. In particular, photo-resist is attacked by ClF_3 in a way that is practically not measurable, so that on the one hand it is particularly easy to passivate parts of a silicon wafer that are not to be etched, while on the other hand very thin passivating layers are already sufficient to ensure complete protection against an etch attack. In many cases, the so-called "native" silicon oxide normally present anyway on silicon surfaces is already able to withstand a chlorine trifluoride attack for several minutes without the silicon underneath it being etched.

A further aspect in the use of ClF_3 and in a limited way also BrF_3 is the generally low reactivity of these highly oxidizing fluorine compounds vis-à-vis silicon, which has the result that an etching performed with them proceeds in a reaction-controlled manner over a wider parameter range and is not limited by a mass transport. This being the case, large undercutting widths can be achieved without a reduction of the etch rate due to a growing aspect ratio of the undercutting channels. With the aid of these gases it is possible, for example, for the lateral extension of the undercutting channels to amount to a multiple, for example 100 to 1000, of their vertical extension.

Finally, isotropic etching using these gases occurs entirely without ion action, which is of great advantage with regard to the desired isotropy and selectivity vis-à-vis non-silicon materials.

On the whole, ClF_3 is in many respects an ideal gas for the selective removal of silicon or porous silicon within the scope of a sacrificial layer technique in that it allows in a very simple manner for the creation of self-supporting membrane structures with minimal restrictions on the freedom of design. In many cases, even a single etch opening is

sufficient in order to achieve a complete undercutting of a membrane area on porous silicon for example.

On the other hand, the disadvantage in the use of ClF_3, and with restrictions also of BrF_3, is the fact that it very easily spreads unchecked via microchannel structures or even nanochannel structures, so that there is a great danger of it creeping extremely quickly behind deposited passivating layers, for example Teflon-like side wall passivating layers in accordance with DE 42 41 045 C1, via micro- or nanocracks in the interface area to the silicon.

Thus it has been shown that a Teflon-like plasma passivating layer produced from C_4F_8 or C_3F_6 has sufficiently many microchannels or nanochannels in the interface area to the silicon below so as to expose, starting from a single opening, for example on the etching ground of the initially produced trench, the entire MEMS structure over a large area to a ClF_3 etch attack in spite of the deposited Teflon-like passivation. A typical defect pattern in this regard is that structures, in which the etching ground was previously cleared of a passivating teflon polymer with the help of ions in accordance with DE 42 41 045 C1, are massively attacked by etching on the entire, generally passivated side wall surface, while structures, in which the etching ground had a remaining, few nanometers thick coating of a Teflon-like polymer, nowhere show signs of an etch attack, even after a long period. The cause of this problem are the microchannels or nanochannels, explained above, in the interface area between the Teflon passivation, which generally adheres poorly to silicon, and the silicon surface, which allow etching gas ClF_3 access to the silicon at undesired places.

The objective of the present invention was to provide a passivating layer on a silicon layer as well as a method for

producing such a passivating layer on a silicon layer, which achieves a reinforced passivation of the interface between the passivating layer and the silicon layer by preventing the formation of, or alternatively by closing, undesired

5   microscale or nanoscale channels, through which otherwise an uncontrolled etch attack, particularly by an isotropically etching gas such as ClF_3 or BrF_3, would occur. In addition it should be possible to integrate the method and the obtained layer system with the passivating layer into plasma etching

10   methods using photo-resist masking for producing trenches and self-supporting structures.

Summary of the Invention

15   The layer system according to the present invention and the method according to the present invention have the advantage over the related art that a very good protection of a silicon layer is thereby achieved, particularly against an etch attack by ClF_3 or BrF_3, and that at least almost no microscale or

20   nanoscale channels are present in the passivating layer, through which one of these gases could attack the protected silicon layer. This being the case, the layer system according to the present invention and the method according to the present invention are particularly suitable for use in the

25   production of at least largely or regionally self-supporting structures in silicon, which temporarily use an anisotropic etching technique, for example according to DE 42 41 045 C1, and temporarily an isotropic undercutting technique, for example according to DE 44 20 962 C2 or DE 198 47 455 A1.

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It is further advantageous that the method according to the present invention and the layer system according to the present invention can be integrated into etching processes that use a photo-resist mask for producing trenches, so that

35   one does not have to fall back on more expensive and more

complex hard material masking which is generally not required in these processes.

Advantageous further refinements of the present invention result from the measures indicated in the dependent claims.
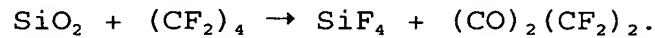
Thus it is particularly advantageous that the problem of a highly oxidizing fluorine compound creeping behind the interface area between the passivating layer and the silicon layer can be prevented especially effectively in that the interface area is first sealed by a thin oxidic passivation which with increasing thickness of the layer is converted into a Teflon-like surface layer with the help of process technology.

Here it must be ensured that such a passivating layer in the sense of a complete sealing layer made of an oxide layer and a Teflon-like layer deposited on top of it on the one hand renders inert all reactive bonding areas of the surface of the silicon layer and makes them unsusceptible to the attack of the highly oxidizing fluorine compounds, and, on the other hand, that it is thick enough to withstand even an etching process of longer duration.

In general, an oxide layer merely 1 nm to 2 nm thin, stemming for example from a plasma oxidation of the surface of the silicon layer, already constitutes a suitable passivation at the atomic level, which would not be susceptible to highly oxidizing fluorine compounds creeping behind it, but which, due to its limited thickness, only briefly withstands an etch attack. In this respect, the attempt to reinforce such an oxide passivation of a silicon surface, which is only a few nanometers thick, directly by a Teflon-like polymer, deposited for example by a plasma, already leads, especially in combination with a usually unavoidable entry of ions on

structure side walls for example, to a damaging of the oxide passivation.

One of many possible undesired etching reactions in connection with the process gas C_4F_8 for the production of Teflon-forming monomers proceeds according to:

$$SiO_2 + (CF_2)_4 \rightarrow SiF_4 + (CO)_2(CF_2)_2.$$

Thus it is often not readily possible to deposit a polymer Teflon-like layer immediately onto an atomic silicon oxide passivation in an at least nearly conformal manner without thereby having to accept damage to, or a removal of, the oxide passivation.

Against this background it is particularly advantageous if, for the sealing or passivation of the silicon layer to be protected, a sequence of layers is used, initially an oxide layer of a thickness of 1 nm to 100 nm, particularly 5 nm to 30 nm, being deposited immediately on the silicon layer or on a silicon oxide surface that is already native or is obtained by plasma oxidation, and, following the production of this layer or the achievement of this thickness of the layer, with the continued growth in the thickness of the passivating layer, a layer being produced by a selective variation of the process parameters, which successively passes over into a Teflon-like layer.

This Teflon-like layer can then be reinforced via the deposition process known from DE 42 41 045 C1 to a layer thickness of for example 30 nm to 800 nm, particularly 50 nm to 400 nm.

Overall, one has thereby advantageously produced over of a primary thin passivation made from an oxide layer a secondary

thick passivation made from a polymer layer, in particular a Teflon-like layer, which can withstand even etching processes of long duration and which has favorable chemical surface properties even vis-à-vis a use of highly oxidizing fluorine compounds such as C_1F_3.

It is further especially advantageous if, as explained, the initially grown first partial layer, especially in the form of an oxide layer, is with progressive layer growth continuously or in discrete steps converted more and more into a polymer partial layer, particularly the Teflon-like layer.

Furthermore it is advantageous that, although silicon oxide layers are usually deposited from a silane such as SiH_4 or TEOS (tetraethyl orthosilicate) or other organic silicon compounds which are incompatible with the chemistry of the Teflon-forming, i.e. for example perfluorinated, monomers, a plasma etching method for silicon is already known from DE 197 06 682 A1, in which an oxide passivation compatible with a fluorine etching chemistry is performed. This process is based on a combination of silicon tetrafluoride and oxygen or N_2O, with the aid of which an oxide film can be built up on a silicon surface, for example on the side walls of trenches.

In addition, a process of this type is not only compatible with a fluorine etching chemistry, in accordance with DE 42 41 045 C1 for example, i.e. with free fluorine radicals or fluorine radicals released in a plasma, but also vis-à-vis Teflon-forming monomers. Although the Teflon-forming monomers, as already explained at the beginning, can result in a degradation of an already produced silicon oxide, which is also utilized in DE 197 06 682 A1 by a continually or intermittently added scavenger gas, it is nevertheless possible to control the relative intensities of the individual reactions of "deposition" or "etching" occurring in the

process through a suitable composition of the process gas with a Teflon-former, silicon tetrafluoride and an oxygen carrier. In addition, a thin silicon oxide layer deposited with the aid of SiF_4 and oxygen or N_2O in accordance with DE 197 06 682 A1

5   is also compatible with a photo-resist masking of a silicon wafer.

Hence it is also especially advantageous if a passivation of a silicon structure or a silicon layer initially begins with an

10   action of a plasma of silicon tetrafluoride and an oxygen carrier on the silicon substrate, the substrate having furthermore been preferably pretreated prior to an O_2 cleaning step in a plasma stripper for the removal of organic residues, for example on side walls, and a subsequent plasma oxidation,

15   for example of side wall surfaces. Following this optional pretreatment, through a reaction of the silicon tetrafluoride with the oxygen carrier, a silicon oxide layer, for example of a thickness of 10 nm to 20 nm, is then grown, as the first partial layer of the passivating layer, on the silicon layer

20   over the surface oxide possibly already natively present or obtained by plasma oxidation. Subsequently, a Teflon-forming monomer-providing gas such as C_4F_8 or C_3F_6, preferably having initially a low gas flow, is added to the plasma.

25   In this manner, first the deposition of the silicon oxide layer on the silicon layer, for example on the side walls of trenches, is slowed down, and afterwards carbon and fluorine are increasingly inserted into the subsequently deposited layer.

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A further increase, continuous or in discrete steps, of the flow of the Teflon-forming, monomer-providing process gas and a corresponding reduction of the flow of the oxygen carrier or oxygen together with the silicon carrier silicon tetrafluoride

35   then causes the deposited or growing layer to become,

continuously or in discrete steps, increasingly Teflon-like,
i.e. it has a gradually decreasing proportion of silicon, SiO
or SiO_2, which is additionally cross-linked in multiple ways
with the produced Teflon filament structures and thereby
5   partly also forms carbidic bonds, i.e. bonds between silicon
and carbon.

If finally only a Teflon-forming, monomer-providing process
gas such as C_4F_8 or C_3F_6 is allowed to enter into the plasma, a
10   pure Teflon film or a Teflon-like film of the structure
$(-CF_2-)_n$ is eventually grown on the transitional layer produced
as explained. Thus an abrupt transition is avoided between the
first, inorganic partial layer of the passivating layer, which
here takes the form of a silicon oxide layer, and the second,
15   polymer partial layer of the passivating layer, which
preferably takes the form of a Teflon-like layer or Teflon
layer. On the contrary, in this manner, a continuous or
graduated transition of the composition of the intermediate
layer between the first partial layer and the second partial
20   layer is produced, which is advantageous especially under the
aspect of an improved adhesion of the Teflon-like partial
layer on the silicon oxide-like partial layer.

Finally, an advantage of the method according to the present
25   invention is the fact that a variation of the process gases
used provides a multitude of different strategies for adapting
the properties of the deposited layers to the requirements of
the individual case. Thus, for example, it is possible to
increase at first only the flow of the Teflon-forming process
30   gas slowly to its final value, while initially still keeping
the flows of silicon tetrafluoride and of the oxygen carrier,
for example oxygen or N_2O, constant, and only subsequently to
reduce, individually or in combination, the gas flows of
silicon tetrafluoride and oxygen or oxygen carrier,

synchronously or in succession, in steps or continuously to zero.

In addition to a particularly good adhesion or chemical bond of the passivating layer on/with the silicon layer, the advantages of a graduated transition or the provision of a graduated layer as an intermediate layer between the first, inorganic partial layer and the second, polymer partial layer also lie in the area of a particularly effective sealing of the silicon layer that is thereby achieved.

Brief Description of the Drawing

The present invention is explained in greater detail by the drawing and the following description. Figure 1 shows a diagrammatic sketch of a section through a layer system that is structured in the form of a trench.

Exemplary Embodiments

An exemplary embodiment of a layer system having a silicon layer and a regionally, superficially deposited passivating layer as well as the method for producing such a passivating layer on a silicon layer is explained with reference to Figure 1. In particular, one initially starts from a silicon wafer, which supports a layer system, suitable for processing in accordance with DE 197 47 455 A1, having buried oxide layers, polysilicon layers and a functional silicon layer, on which a photo-resist masking is deposited, which defines the structures to be produced in the silicon layer.

For this purpose, Figure 1 provides a first silicon layer 10, made of polysilicon for example, on a substrate (not shown) and possibly existing buried oxide layers, on which there is a separating layer 13, made of silicon oxide for example. On

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separating layer 13, a second silicon layer 11 is deposited as a functional silicon layer, on top of which there is a resist mask 12. Figure 1 furthermore shows that with the aid of photo-resist mask 12 regionally a trench 18 was etched into
5   second silicon layer 11, which extends all the way to first silicon layer 10, i.e. it also traverses separating layer 13.

Concretely, following photoprocessing for producing resist mask 12 using the process according to DE 42 41 045 C1, trench
10   18 is etched into second silicon layer 11, which is for example made up of 11 μm thick epipolysilicon. This process stops automatically on separating layer 13 made of an isolation oxide, which according to the teaching of DE 198 47 455 A1 separates functional second silicon layer 11 from first
15   silicon layer 10. In the area of trench 18, the thickness of first separation layer 13 is 50 nm for example. Second silicon layer 11 is used for example for producing self-supporting structures within it.

20   Using a subsequent oxide etching step, separating layer 13 is then initially etched through selectively with respect to silicon and selectively with respect to the photo-resist masking from the trench process according to DE 42 41 045 C1 with the aid of a plasma.
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For this purpose, CHF_3, C_2F_6, C_3F_6, C_4F_8 or a mixture of one of these gases with CF_4 for example are used as a suitable, selectively acting process gas. For the oxide etching step, C_4F_8 or a mixture of C_4F_8 and CF_4 are preferably used. Here, the
30. addition of CF_4 mainly serves to control a polymer formation in the plasma during the etching of separating layer 13, i.e. of SiO_2, although it must be noted that an addition of CF_4 results in a deterioration of the selectivity of the etching of SiO_2 with respect to silicon or photo-resist.
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After separating layer 13 has been etched through and
following a relative stop of the etching process on first
silicon layer 10, first undefined Teflon-like layers on the
side walls or on the bottom of trench 18, as may still be
present from the process according to DE 42 41 045 C1, which
was carried out beforehand, are removed with the aid of an
oxygen plasma. Afterwards the exposed silicon surfaces are
provided in a controlled manner with an oxide that is as dense
as possible, preferably silicon oxide. Here, the initial oxide
is preferably already produced by surface oxidation during the
prior O_2 plasma discharge for removing polymer residues.

To this end, following the plasma etching step for etching
separation layer 13, the wafer having the layer structure in
accordance with Figure 1 is first subjected to a plasma
oxidation, preferably in an O_2 plasma stripper. In the acidic
plasma in the plasma stripper, on the one hand undefined
Teflon-like residues are removed, while on the other hand
accessible silicon surfaces are oxidized, resulting in the
formation of a dense surface oxide.

This "grown" surface oxide on first silicon layer 10 or on
second silicon layer 11 is then first of all reinforced using
a silicon oxide preferably deposited on it immediately
afterwards using the process in accordance with DE 197 06 682
A1, i.e. with the aid of SiF_4 and an oxygen carrier. In this
manner, a first, inorganic partial layer, which in the example
explained is made at least approximately of silicon dioxide
(SiO_2), is formed on the side walls of second silicon layer 11
or on the accessible surface of first silicon layer 10
according to Figure 1 on the surface oxide (SiO_2) previously
produced thereon, which is not shown in Figure 1.

Incidentally, it should be mentioned that, during the removal
of the Teflon-like residues of the preprocess and of the

surface oxidation in the oxygen plasma stripper, resist mask
12 is inevitably partly removed along with it, reducing its
thickness. This is indicated in Figure 1 by a dashed line
representing the greater thickness of resist mask 12 prior to
5   the state according to Figure 1.

In particular, the process must be conducted in such a way
that for the subsequent process now carried out there still
remains a sufficiently thick resist mask 12, i.e. for example
10   a resist mask 12 having a thickness of 200 nm to 500 nm
starting from a resist layer having an original thickness of
1000 nm to 2000 nm.

Afterwards, the wafer is put into a plasma reactor, preferably
15   having a high-density, inductively coupled plasma source in
accordance with DE 199 00 179 C1 as is frequently used for
carrying out the process in accordance with DE 42 41 045 C1.

Subsequently, a second, polymer partial layer 15 is deposited
20   on first, inorganic partial layer 14.

For this purpose, one begins for example with a gas flow of
the process gas SiF_4 of 50 sccm (sccm = cm^3/min at normal
pressure) to 200 sccm, for example 100 sccm, together with a
25   gas flow of oxygen or an oxygen carrier such as N_2O, SO_2, NO_2,
NO, CO2, H2O of 10 sccm to 200 sccm, for example 50 sccm, at a
pressure of for example 10 μbar to 100 μbar, for example 10
μbar to 50 μbar, in the etching apparatus and a plasma power
of 500 Watts to 1000 Watts at the inductive source.
30   Furthermore, the substrate electrode is optionally polarized
with a high-frequency power of 5 Watts to 50 Watts, preferably
15 Watts, in order to compact the initially deposited
inorganic partial layer 14 and to drive fluorine out of it.

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Following a deposition of for example 10 nm silicon oxide, which occurs within 30 s to 1 min, for example C_4F_8 or C_3F_6 is then added as a process gas forming Teflon and providing monomers in the plasma, the gas flow being slowly increased, for example within 30 s to 5 min, preferably within one minute, continuously or in discrete steps, starting from zero up to a final gas flow. The final gas flow preferably lies in the range of 10 sccm to 500 sccm, for example at 50 sccm to 250 sccm. During the time span within which the feeding rate of the Teflon-former is increased, the gas flows of the initially used SiF_4 and of the oxygen carrier may either be synchronously reduced to zero, or these gas flows are initially left constant and are individually or collectively reduced to zero once the set final gas flow of the Teflon-former has been reached. For this so-called "downramping", time spans of 30 s to 5 min, preferably one minute, are suitable as well.

It is possible, of course, to mix the above-mentioned procedures, i.e. to combine the run up or ramp down of individual gases in the etching chamber or to perform these independently of one another, which in each case will result in a different composition of the layer produced on inorganic partial layer 14.

A synchronous run up of the gas flow of the Teflon-forming gas and ramp down of the gas flow of the silicon carrier and oxygen carrier is preferred, the sum of the gas flows of all process gases preferably remaining constant at every moment.

For example, one starts with a flow of 50 sccm of the oxygen carrier and 50 sccm of the silicon carrier as well as 0 sccm of the Teflon-former, the gas flow of the Teflon-carrier gradually being run up and the gas flow of the silicon carrier and of the oxygen carrier being gradually ramped down, so that

the sum of the gas flow of all process gases is always 100 sccm, until finally only a gas flow of the Teflon-former of 100 sccm remains and all other gases are ramped down to a gas flow of 0 sccm. With this procedure, it is also possible to

5   maintain an approximately constant process pressure in the etching chamber without additional measures.

Following the conclusion of this "ramping procedure", the deposition with the aid of the Teflon former, i.e. the

10   production of a Teflon layer or a Teflon-like layer, is continued for a few minutes, for example one minute to five minutes, preferably two minutes, only a Teflon-like film now still being deposited as a secondary passivation on top of the previously produced layer system.

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Afterwards, the passivation of silicon layer 11 by well-adhering passivating layer 14, 15 is completed, sealing the interface area between silicon layer 11 and passivating layer 14, 15 sufficiently well so as to prevent subsequently

20   used highly oxidizing fluorine compounds such as ClF3 from accessing passivated silicon layer 11 and thus to prevent an undesired undercutting of passivating layer 14, 15.

All in all, an optionally thin silicon oxide layer not shown

25   in Figure 1, on which first, inorganic partial layer 14 is located, is initially deposited, by the method explained above, on first silicon layer 10, which is accessible in the area of the bottom of trench 18, as well as on second silicon layer 11, which is accessible in the area of the side walls of

30   trench 18. This partial layer 14 is preferably a silicon oxide layer. On first, inorganic partial layer 14 there is then further an intermediate layer, likewise not shown in Figure 1, which in its surface area adjacent to first partial layer 14 is at least approximately composed as the latter, which in its

35   surface area adjacent to second partial layer 15 according to

Figure 1 is at least approximately composed as second partial
layer 15, and which in its composition passes over,
continuously or in steps, from the composition corresponding
to first partial layer 14 into the composition corresponding
5   to second partial layer 15. To this extent, this intermediate
layer may also be referred to as a gradient layer. On the
intermediate layer there is finally second, polymer partial
layer 15 according to Figure 1, which is preferably a Teflon
layer or a Teflon-like layer, as is produced by a method
10   according to DE 42 41 045 C2.

In the layer structure explained above, as indicated, it is
also possible to dispense with the silicon oxide layer located
between first inorganic partial layer 14 and silicon layers 11
15   or 10, or this is, if inorganic partial layer 14 is
implemented as a silicon oxide layer, indistinguishable or
hardly distinguishable from the latter.

Finally, for producing a self-supporting MEMS structure,
20   beginning from the stage according to Figure 1, passivating
layer 17 present at the bottom of trench 18 is first
selectively penetrated by a comparatively short etching step
using SF_6 or CF_4, C_2F_6, CHF_3, C_4F_8 or a mixture of these gases
with SF_6 as an etching gas with ion support in a plasma at the
25   bottom of trench 18, and subsequently an MEMS structure to be
exposed is isotropically undercut using ClF_3 or BrF_3, i.e. a
highly oxidizing fluorine chemistry. The undercutting may be
time-controlled, or it may be design-controlled by a lateral
boundary of buried polysilicon islands that are to be removed.
30   Following the completion of the undercutting process, the
wafer is taken out of the etching chamber, and remaining
resist mask 12 and remaining Teflon-like parts of passivating
layer 17 are removed by another O_2 plasma stripping.
Furthermore, thin silicon oxide layers may finally be removed
35   by a brief overetching using HF vapor in all those places

where this is desired for reasons of reduced mechanical stress gradients, for example on the underside of an exposed MEMS structure.

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